

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference PA134800/PCT	FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/IB2004/000653	International filing date (day/month/year) 10.03.2004	Priority date (day/month/year) 10.03.2003	
International Patent Classification (IPC) or national classification and IPC C07C7/10, C10G21/16, C07C2/70, C10G65/04, C10G65/12			
Applicant SASOL TECHNOLOGY (PROPRIETARY) LIMITED			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 5 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand 06.01.2005		Date of completion of this report 13.06.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized Officer O'Sullivan, P Telephone No. +31 70 340-4511	



INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/IB2004/000653

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1, 2, 4-21	as originally filed
3	received on 06.05.2005 with letter of 06.05.2005

Claims, Numbers

1-27	received on 06.05.2005 with letter of 06.05.2005
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Drawings, Figures

1-3	as originally filed
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- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/IB2004/000653

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-27
	No: Claims	
Inventive step (IS)	Yes: Claims	1-27
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-27
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following documents:

D1: US-A-6 392 109
D1: WO 02/31085 A
D3: DE 199 11 910 A
D4: US-A-4 686 317

1. Novelty (Art 33(2) PCT)

1.1 D1 discloses an integrated process for the production of alkylbenzenes from syngas. D1 describes an iron-catalysed Fischer-Tropsch reaction used to convert syngas to a high proportion of C₆-C₈ hydrocarbons, which are subsequently used to form aromatic rings and a cobalt-catalysed Fischer-Tropsch reaction in which a high proportion of linear C₁₈-C₂₆ hydrocarbons are produced for use in alkylating aromatics (see D1, column 2, lines 23-41). Other fractions may also be produced (column 16, lines 15-25). The fraction may also be isolated from a single Fischer-Tropsch reactor, for example via fractional distillation. D1 discloses (column 1, lines 53-56) that the fractions are optionally but preferably treated to remove oxygenates by either hydrotreating or *extraction*. Hydrotreating is used in the examples (column 6, lines 18-21 and lines 52-55). The feedstock for the alkylation reaction may contain up to 40% linear olefins (D1, column 16, lines 26-34). In a preferred embodiment of D1 (see D1, column 17, line 51 - column 18, line 5), the reaction products of the alkylation reaction include unconverted paraffins, unconverted aromatics, alkylbenzenes, aromatics with more than one alkyl group and polymers. The aromatics and unconverted paraffins can be obtained via fractional distillation and recycled whereby the paraffins are subjected to dehydrogenation conditions to form a stream containing a mixture of unconverted paraffins, mon-olefins and di-olefins from which the di-olefins are removed.

However, in D1, column 2, lines 63-65 and in Fig 1 it is stated that a C₁₈-C₂₆ fraction from a Fischer-Tropsch reaction is *dehydrogenated* to form C₁₈₋₂₆ olefins which are used to alkylated aromatics. On column 16, lines 33-34 it is stated that the paraffinic C18-26 fraction *must be* converted into olefins, for example, by dehydrogenation chemistry. From

this it appears that the olefins that are subjected to the alkylation reactor are the product of a dehydrogenation reaction, and not the direct products of a Fischer-Tropsch reaction. Also in D1, column 1, line 65 -column 2, line 1, it is stated that the C₁₈₋₂₆ fraction may include sufficient olefins and alcohols such that it can be directly reacted with aromatics to form alkyl benzenes. In this case, the *direct* reaction of the C₁₈₋₂₆ fraction in an alkylation reaction without a dehydrogenation step, *no oxygenated removal step* is suggested. If the oxygenated removal step did take place, the fraction would not include "sufficient olefins and *alcohols*" since the alcohols would have been removed. Accordingly, the combination of taking olefins formed directly in a Fischer-tropsch reaction and subsequently removing oxygenates therefrom according to present claim 1 is not disclosed in D1. Present claims 1-27 may therefore be considered novel according to Art 33(2) PCT.

1.2 D2 discloses a process for separating olefins and paraffins from oxygenates in a liquid hydrocarbon stream (see page 3, paragraph 1- page 4, paragraph 4). The hydrocarbon, which originates from a Fischer-Tropsch process, is first distilled to give, for example, a C₄ to C₁₈ hydrocarbon. The oxygenates are separated therefrom by extraction with a polar solvent which comprises a mixture of water and an organic liquid such as, but not limited to, propanol. The water typically comprises no more than the azeotropic composition of water in the organic liquid. There is no mention of the production of linear alkyl benzenes from the resultant olefin /paraffin stream. Present claims 1-27 can therefore be considered novel over D2.

1.3 D3 (column 1, lines 1-25) discloses the liquid-liquid extraction of oxygenates from a Fischer-Tropsch synthesis hydrocarbon stream. The solvent chosen is a solution of either methanol, ethanol, propanol or butanol in water. There is no mention of the production of linear alkyl benzenes from the olefin/paraffin stream. Present claims 1-27 can therefore be considered novel over D3.

1.4 D4 discloses a process for removing oxygenated impurities from Fischer-Tropsch naphtha and its subsequent oligomerization to produce liquid hydrocarbon fuels. The oxygenates are removed by liquid-liquid extraction using a polar organic solvent, containing a 2-aminoalkanol. Table 2 lists however solvent systems for which the extraction has been tested and the final solvent is 25% MeOH in H₂O. Present claims 1-27

can therefore be considered novel over D4.

2. Inventive Step (Art 33(3) PCT)

As discussed above (1.1), the combination of taking olefins formed directly in a Fischer-tropsch reaction and subsequently removing oxygenates therefrom according to present claim 1 is not disclosed in D1. Where a direct alkylation is suggested in D1, no oxygenate removal step is suggested. This would indicate that the inventors did not believe that it would be possible to remove oxygenates from a Fischer-Tropsch product stream and still have sufficient olefins for an alkylation reaction to form alkyl benzenes. Therefore, the present process does not appear to be suggested by the teaching of D1 and claims 1-27 are considered inventive according to Art 33(3) PCT.

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SUMMARY OF THE INVENTION

According to a first aspect of the invention there is provided a process for producing linear alkyl benzene, the process including the steps of obtaining a hydrocarbon condensate containing olefins, paraffins and oxygenates from a low temperature Fischer-Tropsch reaction;

- a) fractionating a desired carbon number distribution from the hydrocarbon condensate to form a fractionated hydrocarbon condensate stream which is the product of a Fischer-Tropsch reaction;
- b) extracting oxygenates from the fractionated hydrocarbon condensate stream from step (a), advantageously while preserving the olefin/paraffin ratio in the stream, to form a stream containing olefins and paraffins which is the product of a Fischer-Tropsch reaction;
- c) combining the stream containing olefins and paraffins from step (b), which is the product of a Fischer-Tropsch reaction, with the feed stream from step (g) to form a combined stream;
- d) alkylating olefins in the combined stream from step (c) with benzene in the presence of a suitable alkylation catalyst in an alkylation reactor;
- e) recovering linear alkyl benzene from the alkylation reactor;
- f) recovering unreacted paraffins from the alkylation reactor;
- g) dehydrogenating the unreacted paraffins in the presence of a suitable dehydrogenation catalyst to form a feed stream containing olefins and paraffins; and
- h) sending the feed stream containing olefins and paraffins from step (g) to step (c).

Typically, the low temperature Fischer-Tropsch reaction is carried in a slurry bed reactor at a temperature of 160°C - 280°C, preferably 210°C - 260°C, and in the presence of a cobalt catalyst to provide a hydrocarbon condensate containing 60 to 80% by weight paraffins and 10 to 30% by weight, typically less than 25% by weight, olefins. The olefins so produced having a linearity of greater than 92%, preferably greater than 95%. The paraffins so produced have a linearity greater than 92%.

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CLAIMS

1. A process for producing linear alkyl benzene, the process including the steps of obtaining a hydrocarbon condensate containing olefins, paraffins and oxygenates from a low temperature Fischer-Tropsch reaction;
 - a) fractionating a desired carbon number distribution from the hydrocarbon condensate to form a fractionated hydrocarbon condensate stream which is the product of a Fischer-Tropsch reaction;
 - b) extracting oxygenates from the fractionated hydrocarbon condensate stream from step (a) to form a stream containing olefins and paraffins which is the product of a Fischer-Tropsch reaction;
 - c) combining the stream containing olefins and paraffins from step (b), which is the product of a Fischer-Tropsch reaction, with the feed stream from step (g) to form a combined stream;
 - d) alkylating olefins in the combined stream from step (c) with benzene in the presence of a suitable alkylation catalyst in an alkylation reactor;
 - e) recovering linear alkyl benzene from the alkylation reactor;
 - f) recovering unreacted paraffins from the alkylation reactor;
 - g) dehydrogenating the unreacted paraffins in the presence of a suitable dehydrogenation catalyst to form a feed stream containing olefins and paraffins; and
 - h) sending the feed stream containing olefins and paraffins from step (g) to step (c).
2. A process according to claim 1, wherein, in the extraction step b), the ratio of olefins to paraffins is substantially preserved.

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3. A process according to claim 1 or 2 wherein the low temperature Fischer-Tropsch reaction is carried in a slurry bed reactor at a temperature of 160°C - 280°C and in the presence of a cobalt catalyst to provide a hydrocarbon condensate containing 60 to 80% by weight paraffins and 10 to 30% by weight olefins.
4. The process according to claim 3, wherein the Fischer-Tropsch reaction is carried out at a temperature of 210°C - 260°C.
5. The process according to any one of claims 1 - 4, wherein the Fischer-Tropsch reaction is carried out in the presence of a cobalt catalyst.
6. The process according to any one of claims 3 - 5, wherein the hydrocarbon condensate contains less than 25% by weight olefins.
7. The process according to claims 3 - 6, wherein the olefins in the hydrocarbon condensate have a linearity of greater than 92%.
8. The process according to claim 7, wherein the olefins in the hydrocarbon condensate have a linearity of greater than 95%.
9. The process according to any one of claims 1 - 8, wherein the paraffins in the hydrocarbon condensate have a linearity greater than 92%.
10. The process according to any one of claims 1 - 9, wherein the hydrocarbon condensate is fractionated, in step a), into the C₈ to C₁₆ range.
11. The process according to claim 10, wherein the hydrocarbon condensate product is fractionated, in step a), into the C₁₀ to C₁₃ range.

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12. The process according to claim 11, wherein the fractionated hydrocarbon product contains 10 to 30% by weight olefins with a degree of linearity greater than 92%.
13. The process according to any one of claims 1 – 12, wherein the oxygenates are extracted, in step (b), by distillation, dehydration or liquid-liquid extraction.
14. The process according to claim 13, wherein the oxygenates are extracted by liquid-liquid extraction.
15. The process according to claim 14, wherein a light solvent is used in the liquid-liquid extraction.
16. The process according to claim 15, wherein the light solvent is a mixture of methanol and water.
17. The process according to claim 16, wherein the oxygenate extraction process is a liquid-liquid extraction process that takes place in an extraction column using a mixture of methanol and water as the solvent, wherein an extract from the liquid-liquid extraction is sent to a solvent recovery column from which a tops product comprising methanol, olefins and paraffins is recycled to the extraction column, thereby enhancing the overall recovery of olefins and paraffins.
18. The process according to claim 17, wherein a bottoms product from the solvent recovery column is recycled to the extraction column.
19. The process according to any one of claims 16 – 18, wherein the solvent has a water content of more than 3% by weight.
20. The process according to claim 19, wherein the solvent has a water content of from 5% to 15% by weight.

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21. The process according to any one of claims 17 – 20, wherein a raffinate from the extraction column is sent to a stripper column from which a hydrocarbon feed stream containing more than 90% by weight olefins and paraffins and less than 0.2% by weight oxygenates exits as a bottoms product.
22. The process according to claim 21, wherein the hydrocarbon feed stream contains less than 0.02% by weight oxygenates.
23. The process according to any one of claims 1 - 22, wherein the recovery of olefins and paraffins in the hydrocarbon feed stream over the extraction step b) is in excess of 70%.
24. The process according to claim 23, wherein the recovery of olefins and paraffins in the hydrocarbon feed stream is in excess of 80%.
25. The process according to any one of claims 1 - 24, wherein the olefin/paraffin ratio of the fractionated hydrocarbon condensate stream a) is substantially preserved over the extraction step b).
26. The process according to any one of claims 1 - 25, wherein the dehydrogenation reaction at step (g) is carried out at a conversion rate of 10%-15%.
27. The process according claim 26, wherein the fractionated hydrocarbon condensate from step (b) has an olefin concentration of from 10% to 30% by weight, the feed stream from step (g) has an olefin concentration of 10% to 15% by weight, and the combined stream at step (c) has an olefin concentration of 12.5% to 22.5% by weight.